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THE ANALYSIS OF RED FUMING NITRIC ACID
II. DETERMINATION OF WATER BY THE
KARL FISCHER TITRATION

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ABSTRACT

The utilization of the Karl Fischer titration for the direct determination of water in red fuming nitric acid (RFNA) has been investigated, and a modified procedure has been developed whereby water can be successfully determined in RFNA samples containing 0 to 15% nitrogen dioxide. The method controls the experimental variables in order that the following reactions are stoichiometric:

$$H_2O + 2NO_2 \rightarrow HNO_2 + HNO_3$$

$$HNO_2 + \frac{1}{2}I_2 + SO_2 + CH_3OH \rightarrow HI + NO + HSO_4CH_3$$
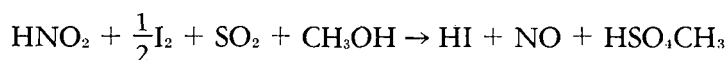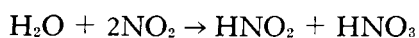
The pooled standard deviation (41 degrees of freedom) is 0.052%, and the absolute error is 0.042%. The method is applicable when hydrofluoric acid and large amounts of metal contaminants are present.

I. INTRODUCTION

It is current practice to obtain the water content of red fuming nitric acid (RFNA) by difference:[a] a series of separate determinations of total acidity, nitrogen dioxide, and metallic impurities is performed, and the results of these determinations are used to calculate the free nitric acid content, the combined nitric acid content, and the nitrogen dioxide content, with water assumed to constitute the remainder.[b] Such a procedure has the obvious disadvantage of being inherently limited in accuracy (0.1%, at the very best) and inapplicable when appreciable amounts of metallic impurities are present owing to their incomplete titration in the determination of total acidity. It is desirable to have available a volumetric procedure for the direct determination of water in RFNA.

The direct determination of water in commercial nitric acid (70% HNO_3) by means of the Karl Fischer reagent was reported about sixteen years ago (Ref. 1). This method has recently been extended to the determination of water in white fuming nitric acid (Ref. 2), but it fails when nitrogen dioxide is present in quantities greater than 1.5% and is, therefore, inapplicable to RFNA.

An investigation of the applicability of the Karl Fischer technique to the determination of water in RFNA was undertaken by this Laboratory, and it was found that the apparent interference of nitrogen dioxide can be circumvented by use of appropriate experimental technique and cognizance of the reaction of nitrogen dioxide with the Karl Fischer reagent. The results of this investigation have led to the development of the first direct volumetric procedure for the determination of water in RFNA. A detailed description of this procedure is given in Sec. III; results obtainable with the procedure are sufficiently accurate to recommend its employ as a referee method of analysis.

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[a] In this Report, RFNA indicates mixtures containing more than 80% HNO_3, 8 to 20% NO_2, and the remainder H_2O. It is realized that the commercial product will contain metallic impurities; RFNA for use in rocketry contains less than 1% HF as corrosion inhibitor.

[b] When HF is present, its contribution to the total acidity has to be taken into account.

II. REAGENTS AND APPARATUS

A. Reagents

The reagents used in this procedure are as follows:

1. Anhydrous nitric acid obtained by room-temperature vacuum distillation from a stoichiometric mixture of sodium nitrate and sulfuric acid. The water content was determined by the Karl Fischer method (Refs. 2 and 3).

2. Anhydrous nitrogen dioxide: The commercial product was stored in a freezer at $-35°C$. A portion of the solid was allowed to melt, and the liquid was used for preparation of samples.

3. Stabilized Karl Fischer reagent; Fischer Scientific Company.

4. Standard water-in-methanol solution prepared by adding weighed quantities of water to anhydrous methanol. The reagent was adjusted to a titer of 2 to 3 mg water per ml.

5. Anhydrous ethylene dichloride: The solvent was first deaerated with nitrogen and then treated with an excess of calcium hydride.

6. Stock water–methylcyclohexane–pyridine solution: This solution was prepared by mixing 500 ml of reagent grade methylcyclohexane, 500 ml of reagent grade pyridine, and 4 ml of water. The solution was deaerated with dry nitrogen for 30 min.

7. Reagent methanol, degassed for 30 min with dry nitrogen.

8. Standardized ceric sulfate solution, about $0.3N$.

9. Ferrous ammonium sulfate solution. $0.1N$.

10. Ortho–phenanthroline indicator solution.

11. Sodium fluoride, reagent grade, dried overnight at $110°C$.

B. Apparatus

The following apparatus is utilized in this procedure:

1. Karl Fischer titration apparatus (Fig. 1) with means for dead-stop end-point indication. A very slow measured stream of dry nitrogen was passed through the titration cell at all times. Oil-pumped nitrogen was first passed through a 3-ft drying tube about 1 in. in diameter packed with anhydrous
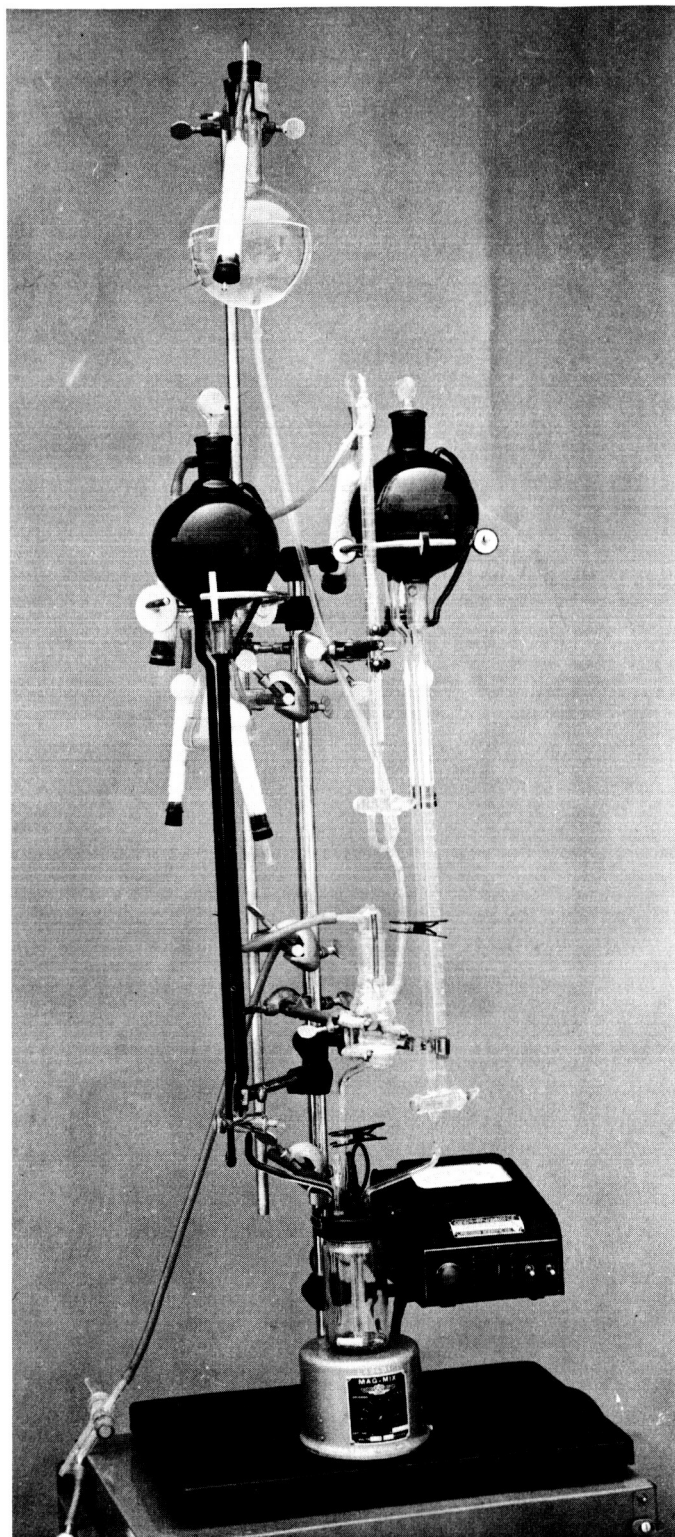

Fig. 1. Modified Karl Fischer Apparatus

magnesium perchlorate and then through a 1-ft by 3-in. trap packed with glass beads kept cool by liquid nitrogen.

2. Polyethylene ware:[c] narrow-mouth screw-cap bottle, 4-oz capacity, with mating conical cap; narrow-mouth screw-cap bottle, 2-oz capacity with a mating conical cap equipped with a ¾-in. length of 6-mm polyethylene tubing sealed on one end. The sealed tubing is to be used to close off the aperture of the conical cap. (See Fig. 2.)

[c]The polyethylene bottles can be obtained from Kern Company, 8639 Venice Boulevard, Los Angeles 34, California. The polyethylene conical caps can be obtained from Industrial Sales Company of California, 9 West State Street, Pasadena 2, California.
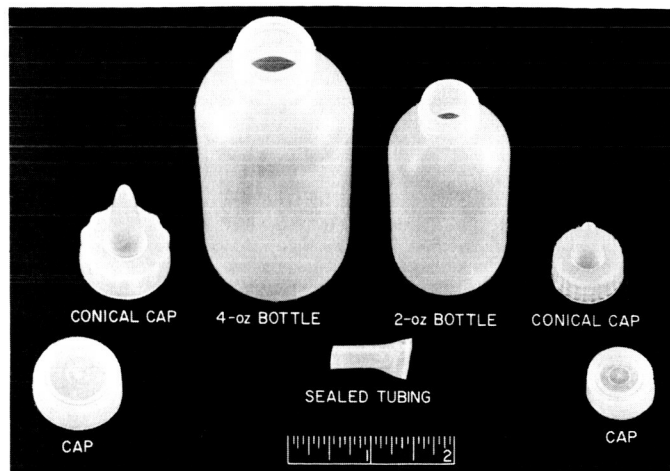

Fig. 2. Polyethylene Ware

III. PROCEDURE

During this investigation, various experimental techniques were evaluated, and a large number of experimental variables were examined. The results of this investigation are embodied in the following recommended procedure:

Take a 2-oz polyethylene bottle equipped with its conical cap and sealed tubing (Fig. 2). Transfer 20 ml of anhydrous ethylene dichloride to the bottle and reweigh to the nearest centigram. With the aid of a 5-ml syringe, add approximately 5 g of RFNA to the polyethylene bottle and redetermine its weight to the nearest centigram. Calculate the weight fraction of RFNA in the ethylene dichloride solution.

Displace the air in a 4-oz polyethylene bottle with dry nitrogen, and, while the nitrogen is still flowing in the bottle, cool it by contact with powdered dry ice. Add to the cold vessel 20.00 ml of anhydrous ethylene dichloride and 10.00 ml of the stock water–methylcyclohexane–pyridine solution. If metallic impurities (e.g., $Fe^{+++} > 1\%$) are present which can consume appreciable amounts of Karl Fischer reagent, 0.1 g dried NaF should be added at this point. This reagent will complex the metal in order that it will not react with the Karl Fischer reagent. Screw the cap on the bottle and place it in the dry ice until the solution is frozen nearly solid. Remove the bottle from the dry ice.

Remove the sealed tubing cap from the 2-oz polyethylene vessel and add, dropwise, approximately 5 g of the RFNA–ethylene dichloride solution to the contents of the 4-oz polyethylene bottle; swirl the contents of the 4-oz bottle while the RFNA solution is being added (pyridinium salts separate). Immediately replace the caps on their respective vessels. Allow the mixture in the 4-oz bottle to stand for 5 min.

Reweigh the 2-oz bottle with its caps. From the weight fraction of RFNA in ethylene dichloride solution and the weight of this solution which was added to the 4-oz bottle, calculate the sample weight of RFNA in the 4-oz bottle.

Dissolve the pyridinium salts in the 4-oz bottle with 10.00 ml of reagent methanol; assist dissolution of the salts by swirling the contents of the capped bottle. Remove the screw cap from the 4-oz bottle and replace it with its conical cap. Squeeze the sides of the bottle and gently force the solution through the conical cap and into a known excess of Karl Fischer reagent in the Karl Fischer titrating vessel. Quickly remove the conical cap, add 5.00 ml of reagent methanol, replace the cap, swirl the contents, and squeeze these contents out into the Karl Fischer titration vessel. Titrate the mixture in the Karl Fischer titration vessel in the usual manner.

A blank determination should be run concurrently with the sample.

Determine the nitrogen dioxide content of the RFNA sample, using a standard procedure; weighed portions of the RFNA sample are added to a known excess of standard ceric sulfate, and the excess ceric sulfate is back-titrated with ferrous ammonium sulfate solution with o-phenalthroline as indicator.

The % water in RFNA is calculated from the following:

$$\% \; H_2O = \frac{mg \; H_2O \; in \; sample \; - \; mg \; H_2O \; in \; blank}{10 \; (g \; RFNA \; sample)} + (0.0978) \, (\% \; NO_2)$$

IV. RESULTS AND DISCUSSION

The success of this and other procedures (Refs. 4 and 5) is predicated on the complete reaction of nitrogen dioxide with a known excess of water introduced at an appropriate point in the experimental procedure and the recognition and control of the reactions of nitrous acid with Karl Fischer reagent.
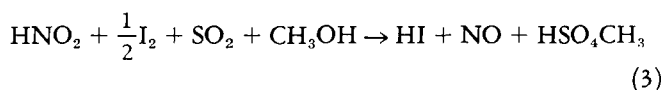
The reaction of nitrogen dioxide with water in the ethylene dichloride solution is

$$H_2O + 2NO_2 \rightarrow HNO_2 + HNO_3 \tag{1}$$
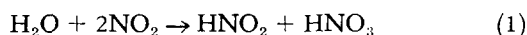
When the reaction mixture is mixed with excess Karl Fischer reagent, the excess water reacts as follows:

$$H_2O + I_2 + SO_2 + CH_3OH \rightarrow 2HI + HSO_4CH_3 \tag{2}$$
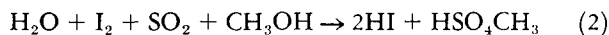
Simultaneously, the nitrous acid formed from Eq. (1) reacts as follows:

$$HNO_2 + \frac{1}{2}I_2 + SO_2 + CH_3OH \rightarrow HI + NO + HSO_4CH_3 \tag{3}$$

When RFNA samples are treated by the experimental procedure described above, the resulting stoichiometry for the determination of water can be interpreted by Eqs. (1), (2), and (3). That is,

$$n_{KF} = n_{H_2O} + n_b - \frac{n_{NO_2}}{4} \tag{4}$$

where n_{KF}, n_{H_2O}, n_b, and n_{NO_2} are the moles of water found by Karl Fischer titration of the sample, the moles of water present in the RFNA sample, the moles of water found by the Karl Fischer titration of the blank, and the moles of nitrogen dioxide present in the sample, respectively.

Table 1 lists the values obtained on synthetic RFNA samples. Table 2 lists the values obtained on synthetic RFNA samples containing hydrofluoric acid. The combined results of both Tables show a pooled standard deviation of 0.049% (26 degrees of freedom), and the average absolute error is 0.030%.

A. Effect of Metallic Impurities

The effect of metallic impurities commonly found dissolved in commercial red fuming nitric acid was examined by addition of hydrated nitrates of these metals to acid samples of known water and nitrogen dioxide content. The water determination of these acids is recorded

Table 1. Karl Fischer Determination of Water in Synthetic Pure RFNA

Prepared Composition %		Indirect Method %		Karl Fischer %	Average %	Standard Deviation	Absolute Error
H₂O	NO₂	NO₂	H₂O	H₂O			
2.12	9.63	9.55	2.28	2.13 2.11 2.05 2.04	2.08	0.04	−0.04
4.77	9.36	9.28	4.65	4.79 4.88 4.75 4.82	4.81	0.05	+0.04
0.12	15.15	15.11	−0.02	0.20 0.10 0.09	0.13	0.06	+0.01
1.19	13.26	13.26	1.56	1.21 1.16 1.28 1.27	1.23	0.06	+0.04
3.38	13.31	13.22	3.53	3.27 3.36 3.33 3.42	3.35	0.06	−0.03
5.09	13.45	13.22	5.08	4.98 5.06 5.04 5.08	5.04	0.04	−0.05

Table 2. Karl Fischer Determination of Water in RFNA Samples Containing HF

Prepared Composition %			Indirect Method %			Karl Fischer %	Average %	Standard Deviation	Absolute Error
H₂O	HF	NO₂	NO₂	HF	H₂O	H₂O			
4.13	0.64	13.40	13.23	0.60	4.16	4.11 4.17 4.19 4.16	4.16	0.03	+0.03
2.37	0.85	14.88	14.76	0.85	2.38	2.44 2.36 2.37 2.39	2.39	0.04	+0.02
3.36	1.05	5.46	5.60	1.11	3.65	3.37 3.29 3.38 3.34	3.35	0.04	−0.01

in Table 3. Ferric salts will be reduced by the SO_2 according to Eq. (5):

$$2Fe^{+++} + SO_2 + H_2O + CH_3OH \rightarrow 2Fe^{++} + 2H^+ + HSO_4CH_3$$
$$(5)$$
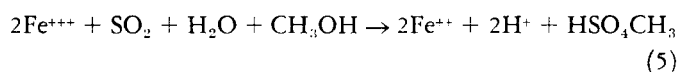
Since one mole of water is consumed for every two moles of ferric salt, it is possible to evaluate quantitatively the effect of ferric salts on the determination of water by the Karl Fischer method. For example, the effect of ferric nitrate on the value of water obtained will be given by:

$$(\% H_2O)_t = (\% H_2O)_i + (0.037) [\% Fe(NO_3)_3] \quad (6)$$

where $(\% H_2O)_t$, $(\% H_2O)_i$, and $[\% Fe(NO_3)_3]$ represent the true percentage of water in RFNA, the percentage of water calculated on the incorrect basis of no interaction between the Karl Fischer reagent and ferric ion, and the percentage of ferric nitrate in RFNA, respectively. According to this relationship, samples containing as much as 1% $Fe(NO_3)_3$ will introduce an error of only −0.04% in the water content. Since RFNA samples generally contain less than 1% $Fe(NO_3)_3$, it is permissible to ignore the presence of the substance. However, it has been found that the addition of 0.10 g of sodium fluoride complexes large amounts of iron to such an extent that ferric ions are not reduced by the Karl Fischer reagent: consequently, this expedient permits the direct determination of water in highly contaminated samples. The other common metallic contaminants such as aluminum, nickel, and chromium do not react with the Karl Fischer reagent.

Commercial RFNA samples do not contain concentrations of metals nearly as large as those examined in

Table 3; hence, it may be concluded that the metals in these acids do not give rise to an interference in the water analysis.

B. Reproducibility

A test of the reproducibility of the method is exhibited in Table 4. A typical commercial RFNA sample containing 14.30% NO_2, 0.59% HF, and 0.02% nonvolatile oxides was analyzed for water with sextuplet replication by two operators. Operator B was experienced with the Karl Fischer technique yet had not previously used the procedure described above. However, his average % water agreed well with that of Operator A. When the weight of acid sample was greater than 0.60 g, the averages and standard deviations determined by the two operators were almost identical.

Table 5 gives an analysis of variance of the data given in Table 4 on the variation within and between operators. The critical value of F, 5% level, is 4.96 (1 and 10 degrees of freedom) (Ref. 6). The calculated value for F is below the critical value; therefore, the agreement between the operator averages is acceptable as measured by the agreement within operators.

C. Sources of Determinate Errors

If the procedure is not followed rigorously, the stoichiometry represented in Eq. (4) may not be valid, and serious errors will result. When the reaction represented by Eq. (1) takes place at room temperature or above,

Table 3. Determination of Water in RFNA Samples Contaminated with Metallic Impurities

Compound Added	Metal Added as Anhydrous Nitrate %	NO$_2$ %	H$_2$O %			Standard Deviation
			Calculated	Found	Average	
Al (NO$_3$)$_3$ • 9H$_2$O	0.541	14.75	2.68	2.60 2.68	2.64	0.06
Ni (NO$_3$)$_2$ • 6H$_2$O	1.96	14.43	3.00	3.00 3.08	3.04	0.06
Cr (NO$_3$)$_3$ • 9H$_2$O	2.07	14.50	3.26	3.15 3.24	3.20	0.06
Fe (NO$_3$)$_3$ • 9H$_2$0	1.37	14.57	2.77	2.77 2.71 2.79	2.76	0.04
	6.12	13.38	5.81	5.60 5.67	5.64	0.05
				5.94[a] 5.78[a]	5.86[a]	0.11
	10.53	12.28	8.62	8.27 8.41	8.34	0.10
				8.78[a] 8.73[a]	8.75[a]	0.04

[a]NaF added in the water determination.
Pooled standard deviation = 0.065%.

HNO$_2$ will undergo either partial or complete disproportionation, i.e.,

$$3HNO_2 \rightarrow 2NO + HNO_3 + H_2O \tag{7}$$

Another complicating factor is the presence of oxygen. If the system is not deaerated, the nitrous acid may undergo partial or complete oxidation, i.e.,

$$HNO_2 + \frac{1}{2}O_2 \rightarrow HNO_3 \tag{8}$$

If either of the side reactions (represented by Eqs. 7 and 8) were stoichiometric, then the correction for nitrogen dioxide in the system would be $n_{NO_2}/3$ and $n_{NO_2}/2$, respectively, instead of the $n_{NO_2}/4$ shown in Eq. (4). Hence, if the proper precautions are not taken, water values will be high and in error by as much as $n_{NO_2}/4$.

In the development of the analytical procedure given above, the possibility of elimination of unwanted reactions by removal of the HNO$_2$ formed in accordance with Eq. (1) was examined. Destruction of HNO$_2$ by addition of sulfamic acid or other substances at appropriate points in the procedure led to nonstoichiometric relationships. Titration in the presence of.sodium acetate and acetic acid, reported by Mitchell and Smith (Ref. 1) as satisfactory for water determinations in the presence of HNO$_2$, was also found to give unsatisfactory results. The

failure of the latter attempt is attributed to the increase in temperature when the solution of pyridinium salts in methanol was added to the acetate buffer.

Table 4. Reproducibility Study of Karl Fischer Method

Operator A		Operator B	
Sample Wt	H$_2$O Found %	Sample Wt	H$_2$O Found %
0.907	2.78	0.603	2.85
1.310	2.76	0.493	3.07*
1.106	2.77	0.938	2.76
1.161	2.78	0.778	2.83
0.837	2.89	0.756	2.76
0.824	2.85	0.661	2.79
			Avg 2.84 ±0.117
Avg 2.81 ±0.053			Avg[a] 2.80 ±0.041

[a]Average omitting * value.

Table 5. Analysis of Variance

Source of Variation	Sum of Squares	Degrees of Freedom	Variance	F
Between operators	0.01275	1	0.01275	1.60
Within operators	0.07968	10	0.00797	
Total	0.09243	11		

Another source of error, already discussed, is the reaction of metallic impurities with Karl Fischer reagent.

Simplification of the described procedure by using a mixture of ethylene dichloride and water–methylcyclo-hexane–pyridine solution instead of two separate dispensations is not practical because the mixture is not stable. Pyridine slowly dehydrohalogenates ethylene dichloride, and water separates as a layer containing pyridine hydrochloride.

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